CHEM-235 - Midterm Test

PART A: *All three questions in this section must be completed.*

(1). (8 points) The reaction $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$ was investigated at 27°C, and the following data were recorded:

expt	$[NO_2]$/mol dm^{-3}	$[F_2]$/mol dm^{-3}	$-d[NO_2]/dt$/mol dm^{-3}s^{-1}	Reaction rate mol dm^{-3}.s^{-1}
1	1.00	1.00	76	38
2	1.00	2.00	152	76
3	2.00	2.00	304	152
4	4.00	4.00	1216	608

(a) Determine the rate law for this reaction, including the value of the rate constant with proper units.

(b) What is the overall order of this reaction?

(c) Is the form of the rate law for this reaction consistent with a one-step mechanism? Explain briefly.

(d) If this reaction is carried out in a rigid vessel, how would the pressure inside the vessel change as the reaction progresses? Assume that there is negligible temperature change throughout the process.

(2). (8 points) At 600°C, cyclobutane has a half-life of 72 seconds, decomposing to form ethylene:

$$C_4H_8(g) \rightarrow 2C_2H_4(g)$$

If a rigid reaction vessel is filled with cyclobutane such that the initial pressure inside the vessel is 5.0 atm, what will the pressure inside the vessel be after 3 minutes?

(3). (4 points) The decomposition of ammonia in the presence of finely-divided platinum is an example of a zero-order reaction.

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \qquad \text{rate} = k$$

Using a simple illustration, explain why the rate of this reaction is independent of the concentration of ammonia. What are the units of the rate constant for this reaction?

PART B: Complete either question 4 or question 5. If both questions are completed, only question 4 will be graded.

(4). (15 points) Based on the collision theory of reaction rates, it can be argued that the rate of the reaction A + B → Products can be estimated using the following equation:

$$\frac{d[A]}{dt} = PL\sigma\sqrt{\frac{8k_bT}{\pi\mu}}\ \exp\left(-\frac{E_a}{RT}\right)[A][B]$$

In your responses to the following questions, you may, but are not required to, refer to this equation.

- *(a) Briefly describe three variables that influence the rate of a reaction and relate them to the key requirements that must be satisfied for a reaction to occur as defined by the collision theory of reaction rates.*
- *(b) What are some limitations of the collision theory of reaction rates? For what kinds of reactions does collision theory provide the best predictions of reaction rates?*

(5). (15 points) Consider the following bimolecular reaction, for which the pre-exponential factor and activation energy are, respectively, $2 \times 10^8\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and $44\ \mathrm{kJ\,mol^{-1}}$:

$$CH_3(g)\ +\ C_2H_6(g)\ \rightarrow\ CH_4(g)\ +\ C_2H_5(g)$$

- *(a) Calculate the enthalpy, entropy and Gibbs energy of activation for this reaction at 25 °C. Rationalise the sign of the entropy of activation in terms of the nature of the transition state for this reaction.*
- *(b) Determine the standard Gibbs energy change for this reaction given that the standard enthalpies of formation of CH_3, CH_4, C_2H_5 and C_2H_6 are 144, -74.9, 111 and -84.5 kJ $\mathrm{mol^{-1}}$ respectively, and the standard molar entropies of CH_3, CH_4, C_2H_5 and C_2H_6 are 194, 186, 248 and 230 $\mathrm{J\,mol^{-1}K^{-1}}$ respectively.*
- *(c) What is the activation energy of the reverse reaction?*
- *(d) Sketch a Gibbs energy diagram for this reaction, indicating on your diagram the reactants, the products and the activated complex.*

Midterm Test: Solutions.

Part A:

Q1.(a) $\text{rate} = v = k[NO_2]^{\alpha}[F_2]^{\beta}$

Determine β by comparing rates in first two rows.

$$\frac{v_2 = \cancel{k}(1.00\ \text{mol}\ \cancel{dm^{-3}})^{\alpha}(2.00\ \text{mol}\ \cancel{dm^{-3}})^{\beta} = 152\ \text{mol}\ \cancel{dm^{-3}}\ s^{-1}}{v_1 = \cancel{k}(1.00\ \text{mol}\ \cancel{dm^{-3}})^{\alpha}(1.00\ \text{mol}\ \cancel{dm^{-3}})^{\beta} = 76\ \text{mol}\ \cancel{dm^{-3}}\ s^{-1}}$$

$$\frac{v_2}{v_1} = (2.00)^{\beta} = 2.0 \qquad \therefore \beta = 1$$

Determine α by comparing rates in second and third rows.

$$\frac{v_3}{v_2} = \frac{\cancel{k}(2.00)^{\alpha}\cancel{(2.00)}}{\cancel{k}(1.00)^{\alpha}\cancel{(2.00)}} = \frac{304}{152}$$

$$(2.00)^{\alpha} = 2.00 \qquad \alpha = 1$$

k can be determined from the concentrations and corresponding rate for any of the four experiments. Using the first:

$$v_1 = 76\ \text{mol}\ dm^{-3}\ s^{-1} = k(1.00\ \text{mol}\ dm^{-3})(1.00\ \text{mol}\ dm^{-3}$$

$$k = \frac{76\ \text{mol}\ \cancel{dm^{-3}}\ s^{-1}}{\text{mol}^{2}\ dm^{\cancel{-6}\,-3}} = 76\ dm^{3}\ \text{mol}^{-1}\ s^{-1}$$

$$\therefore \text{rate} = v = 76\ dm^{3}\ \text{mol}^{-1}\ s^{-1}[NO_2][F_2]$$

(b). This reaction is second order overall.

(c). The form of this rate law is not consistent with a one step mechanism. If the reaction were a one step process, the rate law would have the form

$$\text{rate} = k[NO_2]^2[F_2]$$

and be third order overall, because the one step mechanism would entail the simultaneous collision of three reactant molecules (2 NO_2 and 1 F_2). The rate law deduced from experiment is second-order overall (first order in NO_2 and first order in F_2). In any case, the simultaneous collision of three reactant molecules is a highly improbable event, so it would be highly unlikely such a reaction could take place in a single step.

(d). According to the ideal gas relationship, $PV = nRT$. Since V, R and T are constants, ΔP depends only on Δn, the change in the amount of gas.

$\Delta n = 2 - 3 = -1$ in this reaction, so one expects the pressure inside the rigid vessel to decrease as the reaction progresses.

Since the half-life of cyclobutane is independent
Q(2) of cyclobutane concentration, this reaction is first-order in cyclobutane.

For a first-order process,

$$\ln P_{C_4H_8} = -kt + \ln P_{0,\,C_4H_8}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{72\ s} = 0.009627\ s^{-1}$$

Initially, the pressure inside the vessel is due entirely to the C_4H_8, and therefore $P_{0,\,C_4H_8} = 5$ atm

After 3 minutes ($= 3\ \text{minutes} \times \frac{60\ \text{seconds}}{\text{minute}} = 180\ \text{seconds}$.

$$\ln P_{C_4H_8} = -0.009627\ s^{-1}(180\ s) + \ln(5.0\ atm)$$

$$P_{C_4H_8} = (5.0\ atm)\, e^{-0.009627\ s^{-1}(180\ s)}$$

$$= 0.88\ atm.$$

To determine the total pressure inside the vessel after 3 minutes, we must remember

$$P_{tot} = P_{C_4H_8} + P_{C_2H_4}$$

We must therefore consider the changes in the partial pressure of both C_4H_8 and C_2H_4

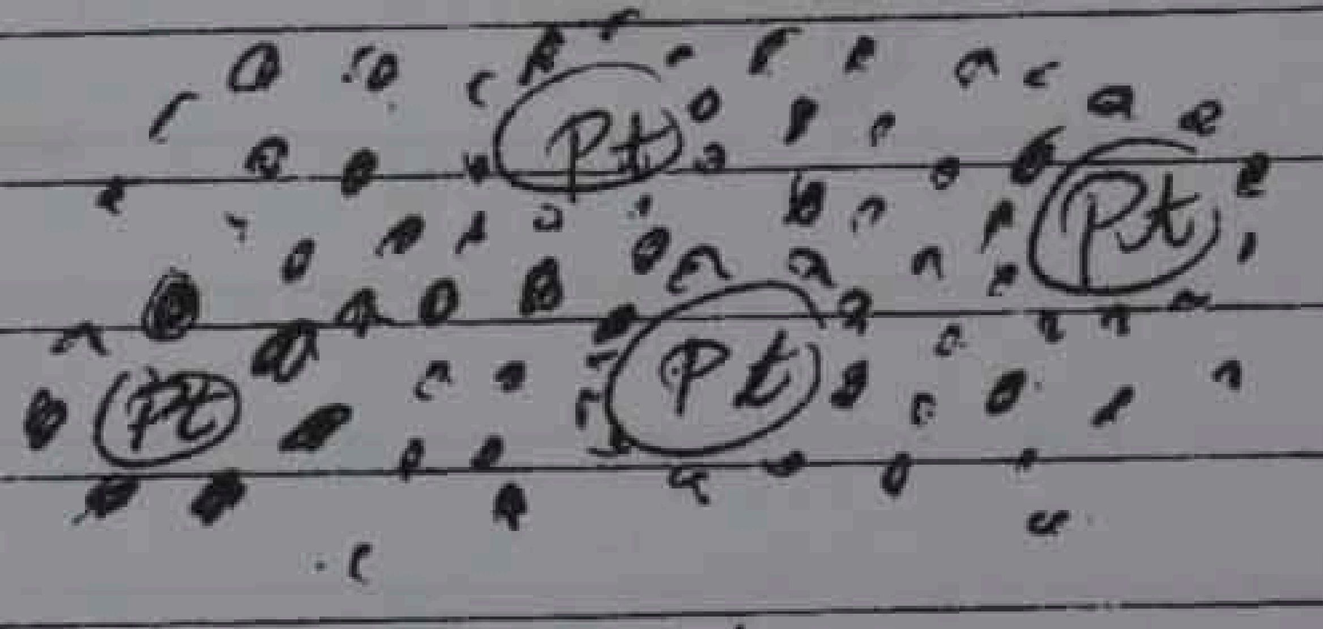
	$C_4H_8 \longrightarrow$	$2C_2H_4$
initial	5.0 atm	0 atm
change between 0 + 3 m.n	(0.88 − 5.0) atm = −4.1 atm	8.2 atm
	0.88 atm	8.2 atm

at 3 minutes

$$P_{tot\ at\ 3min} = 0.88\ atm + 8.2\ atm$$

$$\boxed{= 9.1\ atm}$$

Q3: The decomposition of NH_3 takes place on the surface of the platinum particles. Since there are far more NH_3 molecules than available spots on the surface of the platinum particles, the rate of the reaction will depend entirely on the rate at which ~~the ammonia molecules~~ space becomes available for the ammonia molecules on the platinum surface, which is independent of the number of NH_3 molecules available (unless of course you have very few NH_3 molecules, i.e. fewer NH_3 molecules than available space on platinum surface)



● = NH_3

Only small fraction of NH_3 can access Pt surface at any time

The rate constant would have the same units as the rate (concentration units / time units)

Q 4 According to collision theory of reaction rates,
(a) Three variables that can influence the rate of the reaction

$$A + B \rightarrow \text{Products}$$

are ① The collision density: the number of [A, B] collisions per unit volume per unit time (molecules must collide with each other to react)

② The energy of the collision (Molecules must collide with sufficient energy for the reaction to take place. If energy is less than the activation energy, no reaction takes place).

③ The fraction of collisions with the proper orientation to ~~react~~ react (If molecules c not collide with the proper orientation, n reaction takes place, even if the energy is sufficient).

$$\frac{d[A]}{dt} = \underbrace{P}_{\substack{③ \\ \text{fraction} \\ \text{of} \\ \text{collisions} \\ \text{with} \\ \text{proper} \\ \text{orientation}}} \underbrace{L\,\sigma\sqrt{\frac{8k_BT}{\pi\mu}}\,[A][B]}_{\substack{① \\ \text{Collision} \\ \text{density}}} \underbrace{\exp\left(\frac{-E_a}{RT}\right)}_{\substack{\text{fraction of} \\ \text{collisions} \\ \text{with} \\ \text{sufficient} \\ \text{energy for} \\ \text{reaction}}}$$

(b) Some limitations of collision theory are:

① Molecules are treated as rigid spheres that lack structure. As such, there is no ~~accoun~~ rigorous treatment of orientation effects on the outcome of the collision (reaction /no reaction). Orientation effects are instead treated by introducing a steric factor P to account for the fraction of collisions having the proper orientation for reaction.

② Lack of a rigorous method for the calculation of P

③ Does not provide a satisfactory treatment of reactions taking place in solution.

Collision theory works best for reactions involving simple molecules in the gas phase

5(a). The Gibbs energy of activation, $\Delta^{\ddagger}G^{\circ}$ for this reaction can be calculated from the rate constant with the following equation:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta^{\ddagger}G^{\circ}}{RT}}$$

, where k can be obtained from the pre-exponential factor and activation energy using Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

$$k = 2\times10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\,e^{-\frac{44000\,\text{J/mo}}{(8.3145\,\frac{\text{J}}{\text{mol K}})(298\,\text{K}}}$$

$$= 3.913796\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

$$\Delta^{\ddagger}G^{\circ} = -RT\ln\left(\frac{k\,h}{k_B T}\right)$$

$$\Delta^{\ddagger}G^{\circ} = -\left(8.3145\,\frac{\text{J}}{\text{mol K}}\right)(298.15\,\text{K})\ln\left(\frac{\frac{3.913796\,\text{dm}^3}{\text{mol s}}\times\frac{1\,\text{mol}}{\text{dm}^3}\times 6.626\times10}{(1.381\times10^{-23}\,\frac{\text{J}}{\text{K}})(298.15\,\text{K})}\right)$$

$$= 70\,\text{kJ/mol}$$

The entropy of activation $\Delta^{\ddagger}S^{\circ}$ can be calculated from the pre-exponential factor ~~as~~ from the equation

$$A = e^2\left(\frac{k_B T}{h}\right)e^{\frac{\Delta^{\ddagger}S^{\circ}}{R}}$$

$$\Delta^{\ddagger}S^{\circ} = R\ln\left(\frac{A\,h}{e^2 k_B T}\right) =$$

$$= 8.3145\frac{J}{mol\,K}\ln\left(\frac{\left(\frac{2.0\times10^{8}\,\cancel{dm^3}}{\cancel{mol}\,\cancel{s}}\right)\left(\frac{1\,\cancel{mol}}{\cancel{dm^3}}\right)6.626\times10^{-34}\,\cancel{J}\,\cancel{s}}{e^{2}\left(1.381\times10^{-23}\,\frac{\cancel{J}}{\cancel{K}}\right)(298.15\,\cancel{K})}\right)$$

$$= \boxed{-103\ J/mol\,K}$$

The enthalpy of activation $\Delta^{\ddagger}H^{\circ}$ can then be obtained from the definition of ΔG

~~$\Delta G^{\circ\ddagger} =$~~

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}H^{\circ} - T\Delta^{\ddagger}S^{\circ}$$

$$\text{or } \Delta^{\ddagger}H^{\circ} = \Delta^{\ddagger}G^{\circ} + T\Delta^{\ddagger}S^{\circ}$$

$$= 69642.48\,\frac{J}{mol} + 298.15\,K\left(-102.6345\,\frac{J}{mol\,K}\right)$$

$$= \boxed{39\ \frac{kJ}{mol}}$$

Note that $\Delta^{\ddagger}S^{\circ}$ is < 0 meaning that the entropy decreases upon formation of the activated complex from reactants. The negative $\Delta^{\ddagger}S^{\circ}$ for this reaction is a reflection of the fact that two reactant molecules cluster together ~~during~~ the in the activated complex as the unpaired electron of CH_3 begins to abstract a hydrogen atom from C_2H_6. The pairing and orienting of the two reactant molecules in the course of activated complex formation reduces the modes of motion available for energy to be dispersed into, resulting in a lower entropy in the activated complex relative to reactants.

(b) $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

$\Delta_r H^\circ = \Delta_f H^\circ(CH_4) + \Delta_f H^\circ(C_2H_5) - \Delta_f H^\circ(CH_3) - \Delta_f H^\circ(C_2H_6)$

$= (-74.9 + 111 - 144 - (-84.5))$ kJ mol^{-1}

$= -23.4$ kJ mol^{-1}

$\Delta_r S^\circ = S^\circ(CH_4) + S^\circ(C_2H_5) - S^\circ(CH_3) - S^\circ(C_2H_6)$

$= (186 + 248 - 194 - 230)$ J mol^{-1} K^{-1} $= 10$ J mol^{-1} K^{-1}

$\Delta_r G^\circ = -23.4$ kJ mol^{-1} $- 298.15\,K\left(10\,J\,mol^{-1}K^{-1} \times \frac{1\,kJ}{1000\,J}\right)$

$= \boxed{-26\ kJ\ mol^{-1}}$

(c). Remember that $\boxed{\Delta_r H^\circ = \Delta^{\ddagger} H^\circ(\text{forward}) - \Delta^{\ddagger} H^\circ(\text{revers}}$

For a bimolecular reaction, $E_a = \Delta^{\ddagger} H^\circ + 2RT$,

so $E_a(\text{forward}) = \Delta^{\ddagger} H^\circ(\text{forward}) + 2RT$

$E_a(\text{reverse}) = \Delta^{\ddagger} H^\circ(\text{reverse}) + 2RT$

and $\Delta^{\ddagger} H^\circ(\text{forward}) = E_a(\text{forward}) - 2RT$

$\Delta^{\ddagger} H^\circ(\text{reverse}) = E_a(\text{reverse}) - 2RT$

Substitution into the boxed equation results in

$\Delta_r H^\circ = E_a(\text{forward}) - 2\cancel{RT} - E_a(\text{reverse}) + 2\cancel{RT}$

$$\Delta_r H^\circ = E_a(\text{forward}) - E_a(\text{reverse})$$

$$E_a(\text{reverse}) = E_a(\text{forward}) - \Delta_r H^\circ$$

$$= 44\ \text{kJ mol}^{-1} - (-23.4\ \text{kJ mol}^{-1})$$

$$\boxed{E_a(\text{reverse}) = 67.4\ \text{kJ mol}^{-1}}$$

(d)